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(71) Applicant *(for all designated States except US)*: TECHNISCHE UNIVERSITEIT DELFT [NL/NL]; Julianalaan 134, NL-2628 BL Delft (NL).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : SIE, Swan, Tiong [NL/NL]; Laan van Vogelenzang 8, NL-1217 PH Hilversum (NL). CYBULSKI, Andrzej [PL/NL]; Westeinde 93, NL-2275 AC Voorburg (NL). MOULIJN, Jacob, Adriaan [NL/NL]; 2e Sweelinckstraat 144, NL-2517 HB Den Haag (NL).

(74) Agent: SMULDERS, Th., A., H., J.; Vereenigde Octrooibureaux, Nieuwe Parklaan 97, NL-2587 BN The Hague (NL).

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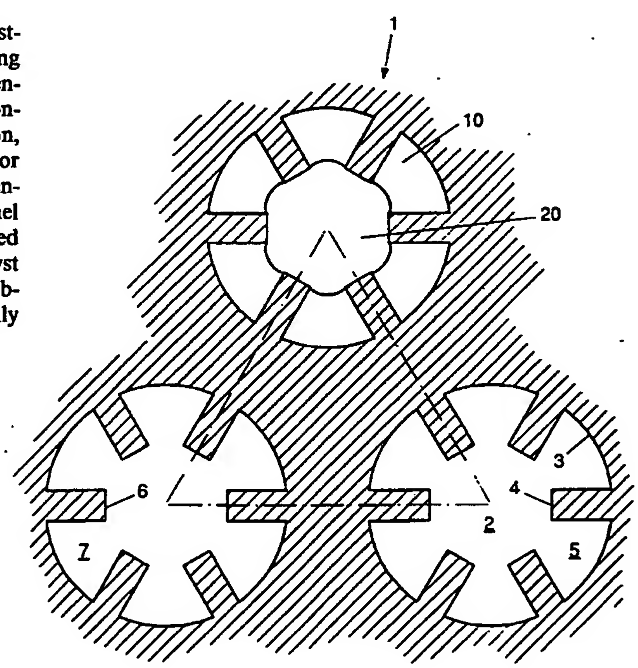
(57) Abstract

There is described a catalyst element (1) consisting of an integral whole having channels (2) extending therethrough. These channels (2) have, in circumferential sense of the cross section thereof, at least one concave wall portion and at least one convex wall portion, preferably provided by longitudinal projections (4) or grooves (7). As a result, a liquid phase (10) will preferentially be located in cavities (5) defined along the channel walls, and a gas phase (20) will preferentially be located centrally in the channels (2). Consequently, the catalyst element (1) according to the invention offers the possibility of being operated in countercurrent mode with only a slight loss of pressure.



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Title: Catalyst element, reactor comprising such catalyst element, die for producing such catalyst element, and method for the hydrogenating conversion of an oil.

The invention relates to a catalyst element suitable for use in reactions between at least one gas and at least one liquid.

The invention particularly relates to such catalyst element for treating oil products, such as for instance the desulfurization of heavy oil by means of hydrogen gas, for which reason the invention will be explained hereinafter with reference to this practical example but, is is emphasized that the invention is not limited to this use.

In practice, desulfurization of heavy oil by means of hydrogen gas takes place in a reactor filled with granular catalyst material. Accordingly, each separate catalyst element has the shape of a granule and can for instance have the shape of a sphere, an elongate cylinder or a flat cylinder (pill). The catalyst granules are dumped in a random manner, and the mutually supporting catalyst granules define a capricious pattern of passageways therebetween. The heavy oil and the hydrogen gas are pressed through these passageways and react with each other, the material of the granules playing a catalyzing part.

This involves various problems.

A first problem concerns the size of the separate catalyst granules. The greater the granules are chosen to be, the smaller the available exterior catalyst surface area in proportion to the catalyst volume or catalyst weight. If the catalyst material consists of a porous support including the active catalyst, this means that in the case of greater granules it becomes increasingly difficult to allow the active catalyst located in the interior of the catalyst granules to contribute efficiently to the reaction (diffusion limitation) to be catalyzed. Hence, a

greater dimension of the catalyst granules is accompanied by a reduced efficiency.

However, the smaller the granules are chosen to be, the greater the flow resistance of the catalyst bed. Given the same yield, this means a greater pressure drop over the catalyst, which is synonymous with a greater loss of energy, and for forcing the substances to be reacted a greater power is needed.

A second problem concerns the manner in which the substances to be reacted can flow through the catalyst material. Due to the relatively great pressure drop over the catalyst material, it is practically impossible, at least for large-scale use, to allow the gas and the liquid to flow countercurrently. A method in which the oil is allowed to drip from the top downwards through the catalyst bed and the hydrogen gas is blown from the bottom upwards, is commercially pointless because of the slight maximum speed that can be used.

Therefore, it is known to present the oil and the hydrogen gas under a relatively high pressure to the reactor and to have them flow through the catalyst bed in the same direction. However, a number of important drawbacks are attached to the operation in such co-current mode, in particular when a gaseous reaction product is formed in the reaction to be catalyzed, such as is the case in the desulfurization of heavy oil by means of hydrogen gas, wherein in fact H_2S is formed. The further the liquid progresses in the reactor, the more it is polluted with that gaseous reaction product, which counteracts the reaction to be catalyzed. Further, the liquid, as it progresses further in the catalyst bed, will increase or decrease in temperature more and more, depending on whether the reaction to be catalyzed is exothermic or endothermic, so that in a commercial reactor provisions have to be made for maintaining the temperature within certain limits.

The object of the invention is to overcome the above-mentioned drawbacks.

In particular, a first object of the invention is to provide a catalyst element whose active catalyst can be used highly efficiently, while yet this catalyst element has only a relatively slight flow resistance.

A further object of the invention is to provide a catalyst element which is in particular suitable for being driven in a countercurrent mode.

To this end, according to the invention, the catalyst element of the above-mentioned type is characterized by at least one channel extending through the catalyst element, the wall of this channel, in circumferential sense of the cross section thereof, having at least one concave wall portion and at least one convex wall portion. Within the scope of the present application, a transition between two wall portions intersecting at an angle smaller than 180° will also be considered to be "concave", and a transition between two wall portions intersecting at an angle greater than 180° will also be considered to be "convex".

In a preferred embodiment, the wall of the channel mentioned comprises at least one longitudinal projection and or at least one longitudinal groove.

It is observed that a catalyst element having a plurality of channels extending therethrough having a smooth wall is known per se. However, this known catalyst element is only suitable for having a gas (mixture) low therethrough, such as for instance in the case where exhaust gas of an internal combustion motor is cleaned. If this known catalyst element was used for having a gas and a liquid flow countercurrently, stagnation phenomena would occur in the channels which would increase the flow resistance and reduce the efficiency.

Because the wall of the catalyst channel according to the present invention comprises at least one longitudinal projection and/or at least one longitudinal groove, a separation between the gas phase on the one hand and the liquid phase on the other is

automatically effected, so that no stagnation occurs and the flow resistance remains low.

The invention will be further explained hereinafter by a description of preferred embodiments of the catalyst element according to the invention, with reference to the drawings. In these drawings:

Fig. 1 shows a section of a portion of the catalyst element according to the invention, which portion comprises three channels;

Fig. 2A-L shows different configuration variants of the channel in a catalyst element according to the invention;

Fig. 3 is a perspective view of a catalyst element according to the invention;

Fig. 4 is a side elevation of a reactor according to the invention; and

Fig. 5 shows a graph for explaining the advantages of a countercurrent mode.

In the figures, identical or comparable parts are designated by the same reference numerals.

Fig. 1 shows a partial section of a catalyst element 1 according to the invention. Fig. 1 shows three channels 2 with a channel wall 3. In a practical embodiment, the catalyst element 1 as a whole may for instance have a rectangular or hexagonal cross section having cross dimensions in the order of for instance 50 cm and the channels 2 may have cross dimensions in the order of approximately 1-10 mm. It will then be understood that the pattern of channels 2 may continue in a "dense packing", although this is not shown separately.

The catalyst element 1 may be produced from a support material, for instance a ceramic material or a metal for a proper heat conduction, on which a thin layer of the actual catalyst material is provided, which layer accordingly forms the boundary surface of each channel. However, in a preferred embodiment which is in particularly suitable for the desulfurization of oil by

means of hydrogen gas, the catalyst element 1 is integrally produced from catalyst material, such as for instance a porous matrix impregnated with active substance. An example thereof is γ-alumina having in at least a part of the pores thereof W, Co, Mo, Ni, or Mn atoms as active substance, or combinations of these atoms.

The channels 2 shown in Fig. 1 have a circular section. The channel wall 3 of each channel 2 comprises six projections 4 extending in the longitudinal direction of the channels 2. Each projection 4 can be considered to be a convex wall portion and each wall portion between adjacent projections 4 can be considered to be a concave wall portion.

As shown in Fig. 1 in only one of the channels shown, the liquid phase 10 will tend to be mainly located in the spaces 5 surrounded by the channel wall 3 and the projections 4. The greater the degree of humidification between the liquid phase 10 and the material of the catalyst 1, the greater this tendency. Centrally in the channel 2, the liquid phase 10 will leave clear space for the gas phase 20. Consequently, the liquid flow and the gas flow do not interfere with each other, so that it is possible to operate the catalyst element 1 in a countercurrent mode in which the liquid phase 10 and the gas phase 20 flow countercurrently, while the pressure drop occurring is only slight.

Various configuration variants are possible, a number of which will be described hereinafter. However, this description should not be considered an exhaustive enmumeration.

The walls of the projections may for instance extend radially (Fig. 2A). However, when the two walls of each projection are parallel to each other, as in the embodiment illustrated in Fig. 1, this offers the advantage that the catalyst material in each projection, calculated in the height direction of that projection, is used equally efficiently.

Channel 2 shown in Fig. 1 has a generally circular section. The channel may also have a polygonal section, such as for instance a triangle (Fig. 2B), a square (Fig. 2C), or a hexagon (Fig. 2D). This hexagonal geometry offers the particular advantage that a relatively high ratio of catalyst material volume to total volume can be realized, and that a relatively great contact surface between catalyst material and liquid phase can be realized.

A capricious shape, as shown in Fig. 2E, is also conceivable, but from a productional viewpoint and in view of the efficiency, a rotation-symmetrical shape for the channels is preferred, although this is not at all necessary for realizing the effect aimed at by the invention.

Also, the projections/grooves do not have to be only a part of the channel wall 3. Fig. 2F shows a variant in which the channel 2 has a triangular section and in which each projection 4 has a triangular section, the base of the projection 4 being as large as the triangle side of the channel 2. In this case, the top of each projection 4 can be regarded as a convex wall portion and the transition between adjacent projections 4 can be regarded as a concave wall portion.

The number of projections 4 per channel 2 can be varied. In the case of the circular section shown in Fig. 1, the number of six projections 4 per channel 2 is preferred for reasons of efficiency, but another number of projections 4, preferably evenly distributed along the circumference of the channel, is also possible. In the case of the polygon shapes illustrated in the Figs. 2B-D and 2F, it is efficient, but not necessary, that the number of projections 4 per channel 2 corresponds to the number of angles of the respective polygon. In this connection, the projections 4 may be positioned in the respective angles of that polygon, as illustrated in the Figs 2C and 2D, but a better surface area/weight proportion is realized when the projections 4

are positioned on the polygon sides and preferably on the center thereof, as illustrated in Fig. 2B.

Hereinabove, the embodiment variant shown in Fig. 1, for instance, is described as a circular cross section having six longitudinal projections 4. However, this embodiment variant can also be described as a hexagonal cross section having walls 6 and having six longitudinal grooves 7 (shaped like a wedge of cake), positioned in six angles. Fig. 2G shows an embodiment variant having a hexagonal cross section and three projections 4, while Fig. 2H shows an embodiment variant having a hexagonal cross section and three grooves 7. A combination of projections 4 and grooves 7 is also conceivable (Fig. 2I).

It is not necessary that the walls of the projections or grooves follow a flat plane, but those walls may also be curved. An example of such configuration is shown in Figs 2E, 2J and 2L.

A particularly efficient use of the catalyst material is realized in a configuration in which the channels 2 comprise projections 4 and grooves 7, and the channels 2 are arranged in the catalyst element 1 in such a manner that the projections 4 and the grooves 7 of adjacent channels 2 mesh with each other. Examples of such a configuration are shown in Figs 2K and 2L. In the embodiment shown in Fig. 2K the channels 2 have a square section. Each time, a rectangular projection 4 is positioned on the center of two opposite walls, while in the two other opposite walls a rectangular groove 7 is provided. Each channel 2 is adjoined by four channels whose orientation is perpendicular to that of channel 2 mentioned. In the embodiment shown the dimensions are chosen to be such that the catalyst walls located between the channels 2 are always equally thick. Further, the dimensions in this embodiment are chosen to be such that the spaces 5 surrounded by the channel wall 3 and the projections 4 are equally large as the grooves 7.

In the embodiment illustrated in Fig. 2L the channels 2 can be represented as having a square section as well. Provided side

by side on each wall are a convex projection 4 and a concave groove 7, whose cross sections in the embodiment illustrated have the shape of a semicircle having a diameter substantially equalling half the side of each square. In this embodiment, too, the dimensions are chosen to be such that the catalyst walls located between the channels 2 are always equally thick. In this construction, the spaces 5 for receiving the liquid phase 10, always surrounded by a groove 7 and portions of the adjacent projections 4, have a sickel-shaped cross section.

In practice, the actual dimensions of the channels 2, the projections 4 and the grooves 7 will be adapted to the material properties of the substances to be fed through, in particular the liquid phase 10. In general, the height of the projections 4 and the depth of the grooves 7 will be chosen to be in the range between 5 and 50% of the relevant radius of the channel in question, with the relevant radius, depending on the configuration in question, been defined as the curvature radius of the channel wall portion at the location of the relevant projection or the relevant groove, or as the distance from that channel wall portion to the geometric center (center of gravity) of the channel in question.

Now, by way of an example, a comparison will be made between on the one hand conventional catalyst elements in the form of extruded cylinders having a length/diameter proportion of 4, and on the other hand a catalyst element 1 according to the embodiment illustrated in Fig. 1.

The conventional granules have for instance a diameter of 1.5 mm and a length of 6 mm. When these granules are dumped in a reactor, a filling degree of ca. 0.6 is realized. In this connection, the filling degree is defined as the catalyst volume/available volume proportion.

Now, of the embodiment illustrated in Fig. 1, the mutual distance between the centers of the channels 2 is designated by L, the diameter of the channels 2 is designated by D, the width

of the projections 4 is designated by x, and the height of the projections 4 is designated by y. In a practical embodiment the following choice can for instance be made:

$$d = 0.8\ L;\ x = \pi/24\ D;\ y = 0.25\ D.$$

In that case, it can be demonstrated in a simple manner that the filling degree is approximately 0.56, which is comparable with the filling degree of the conventional catalyst elements.
In this embodiment, the proportion between the external catalyst surface area and the catalyst volume is approximately 10/L, while in the conventional catalyst elements this proportion is 4.5/d, d referring to the diameter of the conventional catalyst elements. Consequently, when L is chosen to be equal to 3.3 mm, the same proportion between the external catalyst surface area and the catalyst volume is realized as in the conventional catalyst elements.

It can be shown that in this case, in a practical situation, at a channel length of 20 m, a pressure drop for the gas of approximately 0.054 bar will occur, while for the liquid a pressure drop of approximately 0.68 bar will occur. This is a considerable improvement over the conventional situation, where a pressure drop of approximately 4.4 bar will occur under otherwise equal reaction circumstances.

A perspective view of a catalyst element 1 according to the invention with a square cross section is given in Fig. 3. In Fig. 3, the projection/groove structure of the channels 2 is not shown for the sake of simplicity. With the present-day production techniques, it is quite possible to produce this catalyst element with, within reasonable limits, any length and width. However, it is preferred to produce the catalyst element 1 with a standardized length and width, for instance respectively 1 m and 50 cm, and to consider them to be modules with which a reactor 30 having any length and width, for instance respectively 20 m and 5 m, can be filled. Fig. 4 shows a schematic cross section of such a reactor 30, having a supply channel 31 and a discharge

channel 32 for the liquid phase, and a supply channel 33 and a discharge channel 34 for the gas phase. The catalyst elements 1 are oriented such that the channels 2 are vertically directed. The supply channel 33 for the gas phase is arranged at the lower end of the reactor 30, and the gas is blown into it under slightly raised pressure. The supply channel 31 for the liquid phase is located at the top end of the reactor 30, and the pressure drop occurring in the reactor 20 is so small that the liquid can move downwards under the action of gravity.

In this embodiment, as is also shown in Fig. 4, a layer of a granular material 40, for instance conventional granular catalyst material, may be provided between the modules stacked on top of each other, effecting a redistribution and mixture of the reacting substances over the separate channels 2, between two successive layers of modules.

As is also mentioned, the particular advantage of the catalyst element 1 according to the present invention is that due to the intrinsically occurring phase separation in the channels 2, a slight pressure drop occurs, so that on the one hand only a slight pump capacity is needed and, more importantly, a countercurrent operation is possible. The advantages of a countercurrent operation will now be explained with reference to Fig. 5.

Fig. 5 shows in a graphic manner, in arbitrary units, the relation between the concentration of H_2S in the gas phase and the concentration of sulfur (S) in the oil as function of the position in the reactor bed. The first graph (Fig. 5A) relates to a co-current mode, the oil and gas flow being from the left to the right. The second graph (Fig. 5B) relates to a countercurrent mode, the oil flow being from the left to the right and the gas flow being from the right to the left.

As appears from Fig. 5A, the oil in the entrance area of the reactor bed (in Fig. 5A on the left) is in an atmosphere substantially consisting of H_2. However, the H_2S formed during

the desulfurization is entrained with the gas and the oil, so that the concentration of H_2S is relatively great in the greater part of the reactor bed, which counteracts the desulfurization reaction.

On the other hand, in the countercurrent mode, the formed H_2S is entrained by the gas flow to the oil entrance area of the reactor bed and discharged from there. Here, it should be noted that the oil is in fact a mixture of different components having different desulfurization rates. The components that are easiest to desulfurize (greatest desulfurization rate) are already desulfurized in the oil entrance area of the reactor bed. Because of these factors, the concentration of H_2S is relatively great in the oil entrance area and decreases strongly according as the oil progresses further in the reaction bed, such that the average concentration of H_2S is less than in the co-current mode.

A significant consequence hereof is that at the end of the reactor bed in the very pure H_2 atmosphere, the components that are difficult to desulfurize (smallest desulfurization rate) are little obstructed by the counteraction of H_2S, as is indeed the case in the co-current mode. Consequently, the concentration of sulfur in the oil remaining at the end of the reactor bed is considerably less than in the co-current mode. Because at the end of the reactor bed the concentration of H_2S is low, it is moreover possible here to use a catalyst element of a material which is on the one hand particularly active but on the other hand particularly sensitive to sulfur and/or H_2S. Precisely because of this sensitivity, such active catalyst material cannot normally be used in conventional catalyst elements.

Of course, it will be possible to connect two or more reactors in series, with the catalyst materials of the different reactors being mutually different. However, according to a further aspect of the present invention, in a reactor 30 of the type illustrated in Fig. 4, in which a number of modules are stacked on top of each other, the separate modules may have

mutually different compositions, and in particular the modules at the discharge side of the liquid phase may be produced from such particularly active material which is particularly sensitive to sulfur and/or H_2S.

The catalyst element 1 according to the invention can be produced by means of an extrusion process, wherein a starting material is pressed through a die and is subsequently baked. In the extrusion art, it is conventional to produce such die with a high degree of precision while much care is given to the finishing operation of the wall of the extrusion opening to render the surface thereof as smooth as possible. Due to use, the die will wear in course of time and will then require further treatment. However, according to the invention, the wall of the extrusion opening has a certain roughness that is not critical. On the one hand, this simplifies the production of the die, on the other hand, this means that further treatment because of wear will not be necessary, if at all. However, the most important effect of the roughness of the die is that the walls of the extruded channels, in particular of the projections and grooves, will be provided with very small ridges in the longitudinal direction thereof, which ridges will promote the adhesion of the liquid to the channel wall and thereby promote the phase-separating capacity of the channels.

Summarizing, the invention provides a catalyst element which, due to the unique construction of the channels 2, i.e. the combination of concave wall portions and convex wall portions, preferably provided by longitudinal projections 4 or grooves 7, has an intrinsic phase-separating action so that a liquid phase 10 will preferentially be located in cavities 5 defined along the channel walls and a gas phase 20 will preferentially be located centrally in the channels 2. Consequently, the catalyst element 1 according to the invention is pre-eminently suitable for being operated in a countercurrent mode with only a slight loss of pressure.

It will be understood by a skilled person that various modifications are possible with the scope of the present invention. For instance, it is possible to provide a catalyst element with channels having mutually different configurations.

CLAIMS

1. A catalyst element suitable for use in reactions between at least one gas and at least one liquid; characterized by at least one channel (2) extending through the catalyst element, the wall of said channel, in circumferential sense of the cross section thereof, having at least one concave wall portion and at least one convex wall portion.

2. A catalyst element according to claim 1, characterized in that the wall of said channel (2) comprises at least one longitudinal projection (4) and/or at least one longitudinal groove (7).

3. A catalyst element according to claim 2, characterized in that the walls of each projection (4) are parallel to each other, respectively that the walls of each groove (7) are parallel to the opposite walls of the adjacent groove (7).

4. A catalyst element according to claim 2 or 3, characterized in that said channel (2) has a circular section and that the number of projections (4) respectively grooves (7) equals six.

5. A catalyst element according to claim 2 or 3, characterized in that said channel (2) has a section in the shape of a polygon, that the number of projections (4) per channel (2) corresponds to the number of angles of said polygon, and that the projections (4) are positioned on the sides of the said polygon, preferably on the centers thereof.

6. A catalyst element according to at least one of the preceding claims, characterized in that the projections (4) and the grooves (7) of adjacent channels 2 meshed together.

7. A catalyst element according to at least one of the preceding claims, characterized in that the walls of the channels (2), in particular the walls of the projections (4) respectively the grooves (7), are provided with very small ridges extending in the longitudinal direction of the channels.

8. A catalyst element according to at least one of the preceding claims, characterized in that the catalyst element (1) is integrally produced from catalyst material, such as for instance a porous matrix soaked with active substance.

9. A reactor for reacting catalytically therein at least one gas and at least one liquid, comprising at least one catalyst element (1) according to at least one of the preceding claims.

10. A reactor according to claim 9, characterized in that the channels (2) in the at least one catalyst element (1) are vertically directed.

11. A reactor according to claim 9 or 10, characterized in that a supply line (31) for liquid and a supply line (33) for gas are located on both sides of the at least one catalyst element (1).

12. A reactor according to at least one of claims 9-11, characterized in that several catalyst elements (1) are stacked on top of each other.

13. A reactor according to claim 12, characterized in that a distribution layer (40) is located between two of the catalyst elements (1) stacked on top of each other.

14. A reactor according to claim 13, characterized in that the distribution layer (40) contains a granular material, preferably a granular catalyst material.

15. A reactor according to at least one of claims 12-14, characterized in that the catalyst elements (1) of two different layers are produced from mutually different catalyst materials.

16. A process for the hydrogenating conversion of an oil, such as for instance desulfurization, by reacting said oil with a gas under the influence of a catalyst; utilizing a catalyst element (1) according to any one of claims 1-8 and/or a reactor according to any one of claims 9-15.

17. A process according to claim 16, wherein the flow direction of the oil through the catalyst is opposite to the flow direction of the gas through the catalyst.

18. An oil product obtained by means of a process according to claim 16 or 17.

19. A die for the production, by means of an extrusion process, of a catalyst element (1) according to any one of claims 1-8, the wall of the extrusion opening having a certain roughness.

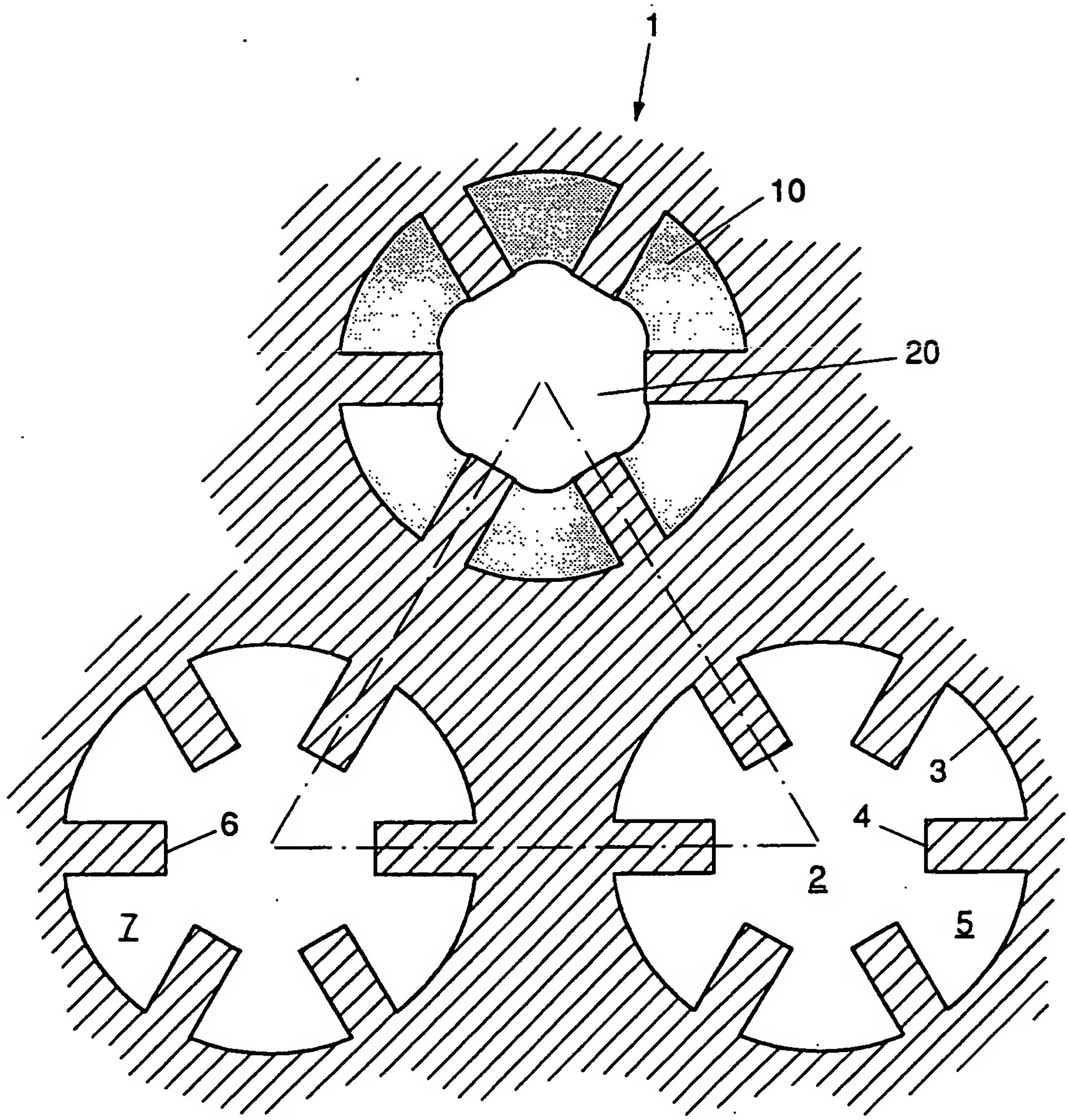

FIG. 1

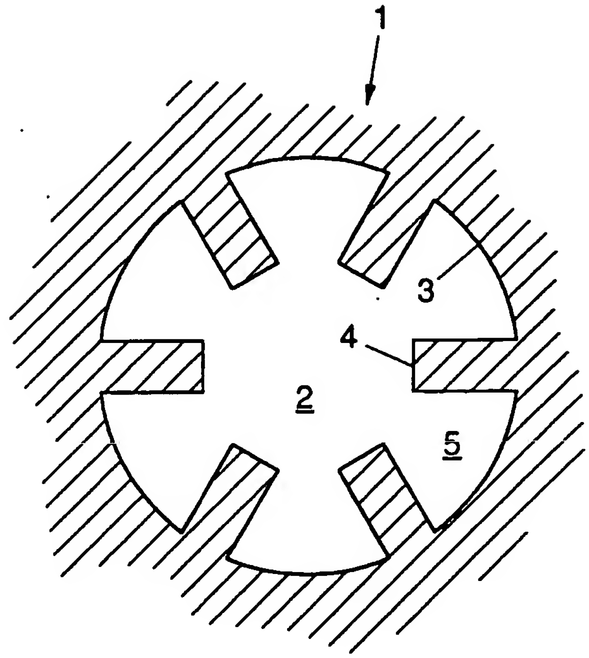

FIG. 2A

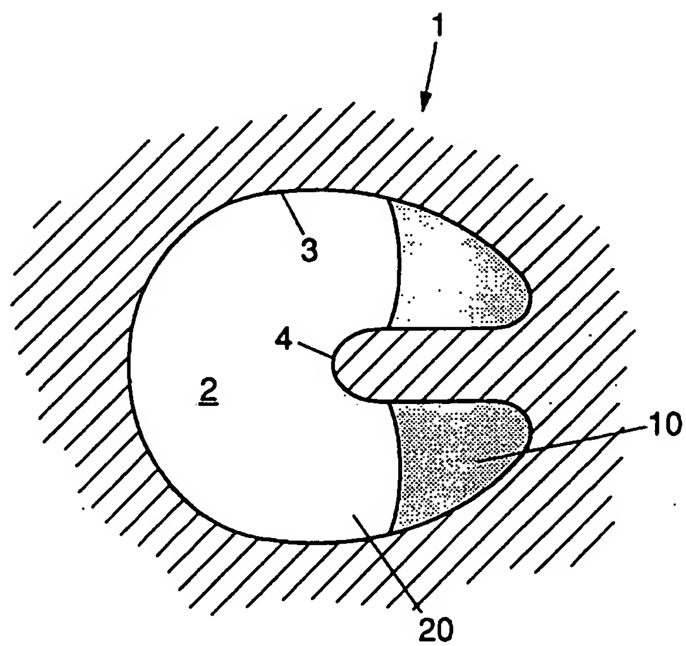

FIG. 2E

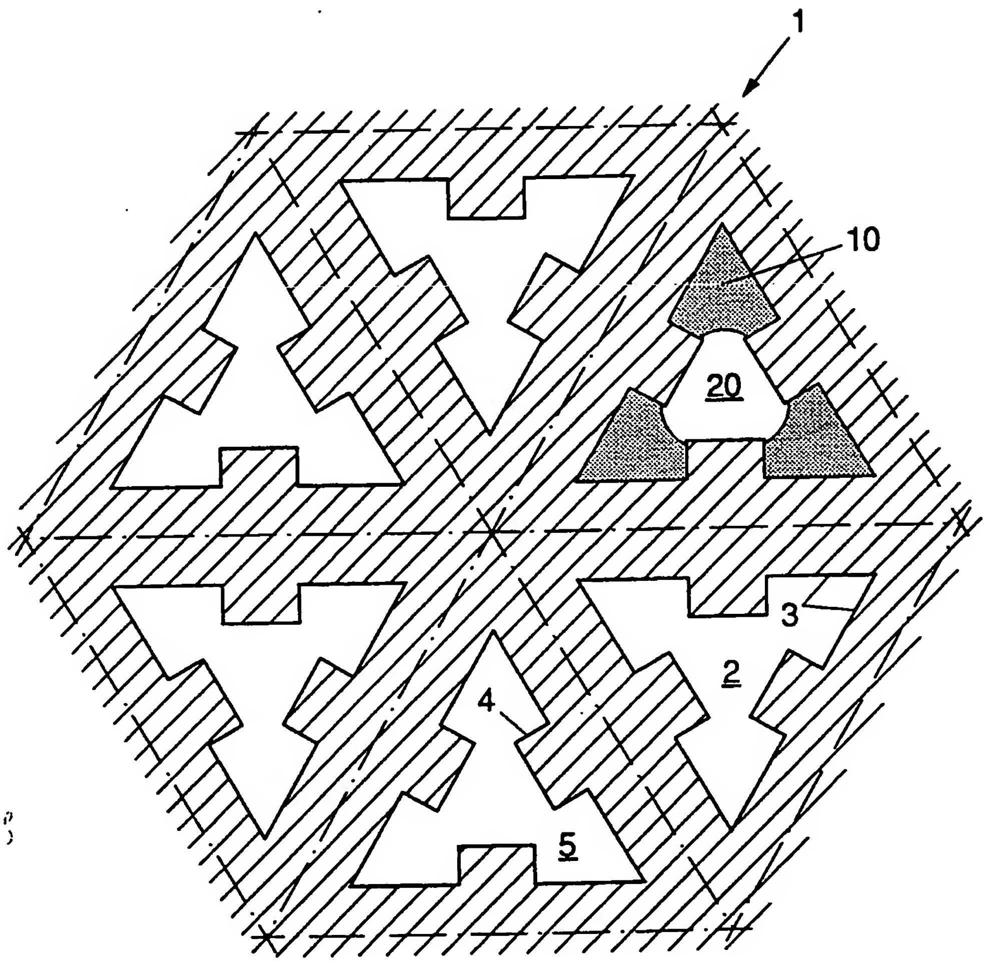

FIG. 2B

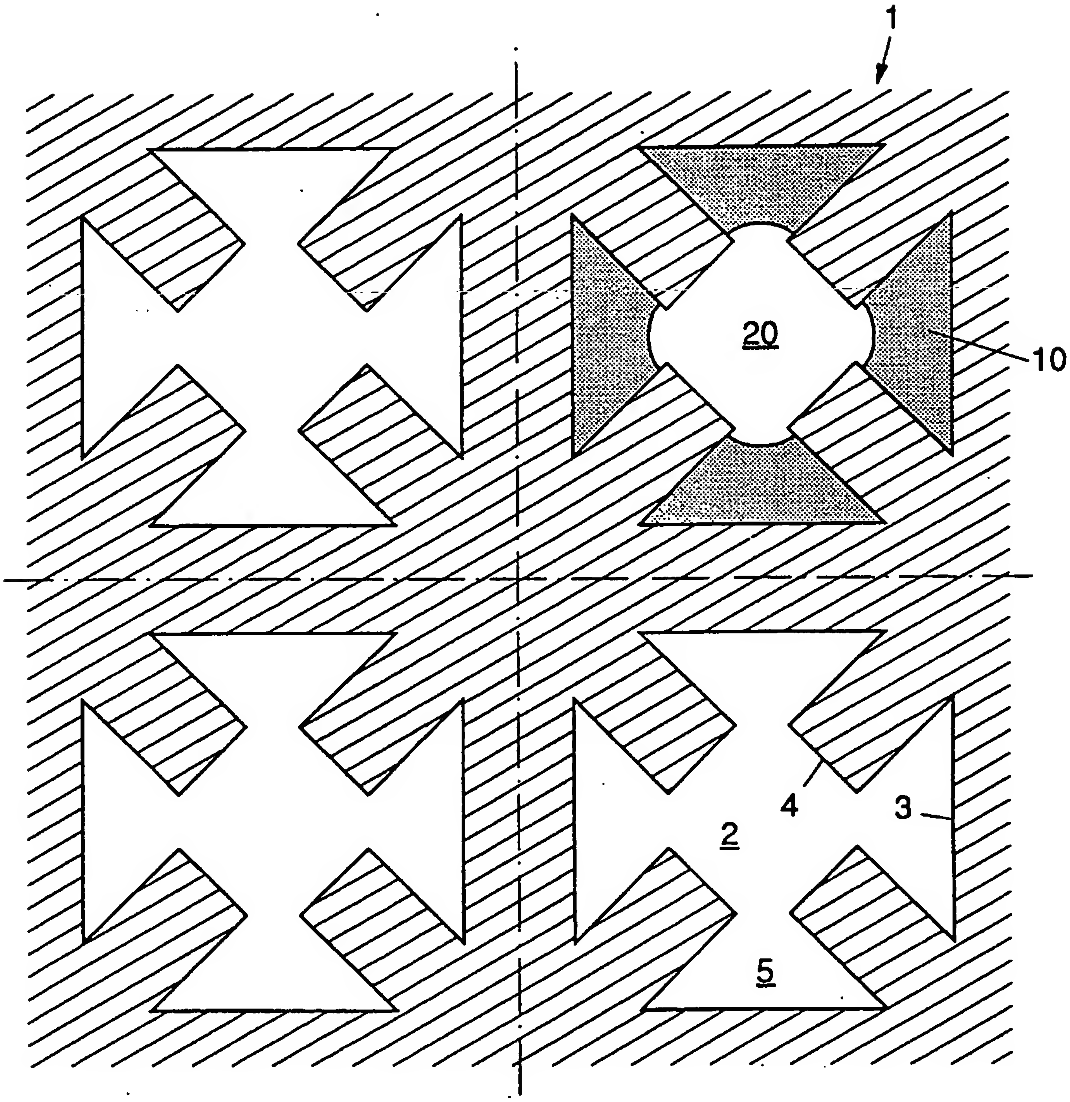

FIG. 2C

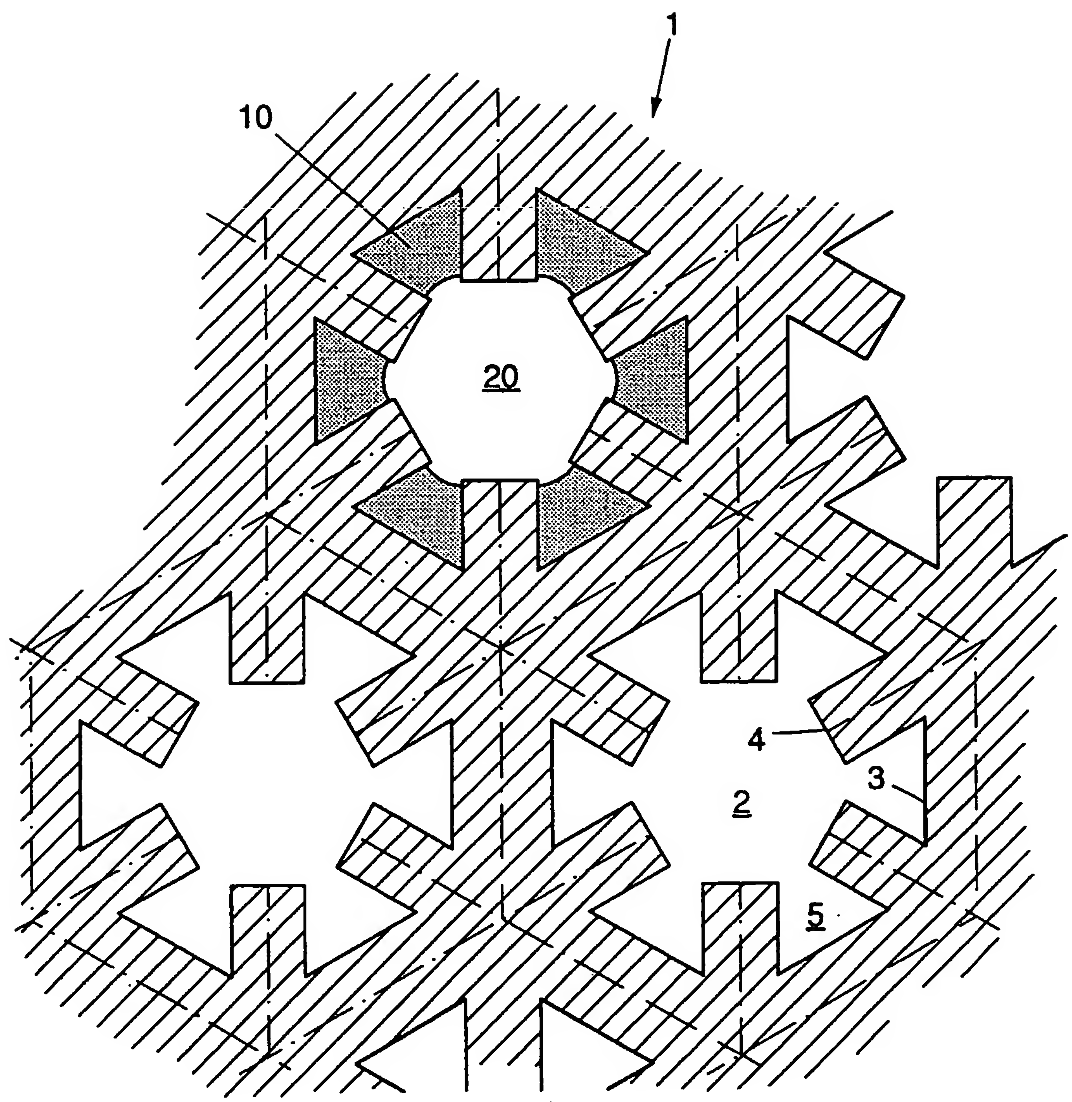

FIG. 2D

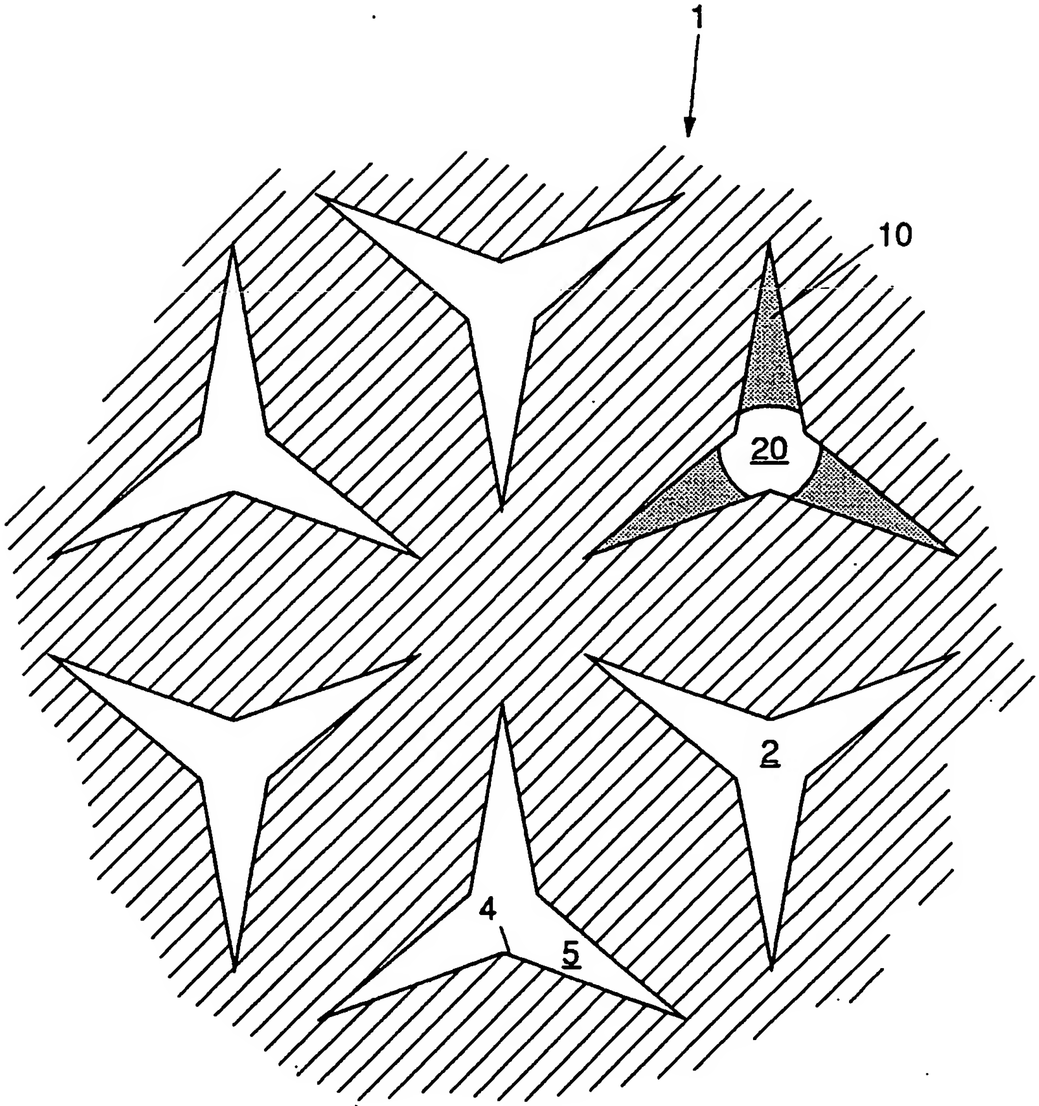

FIG. 2F

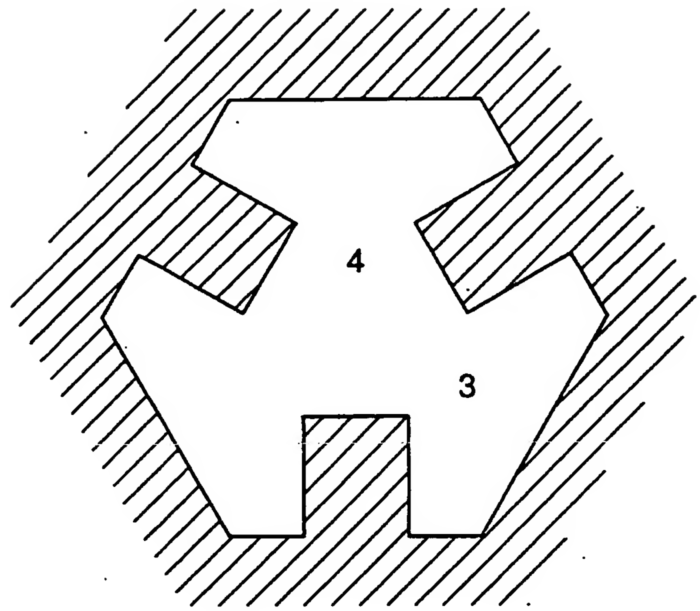

FIG. 2G

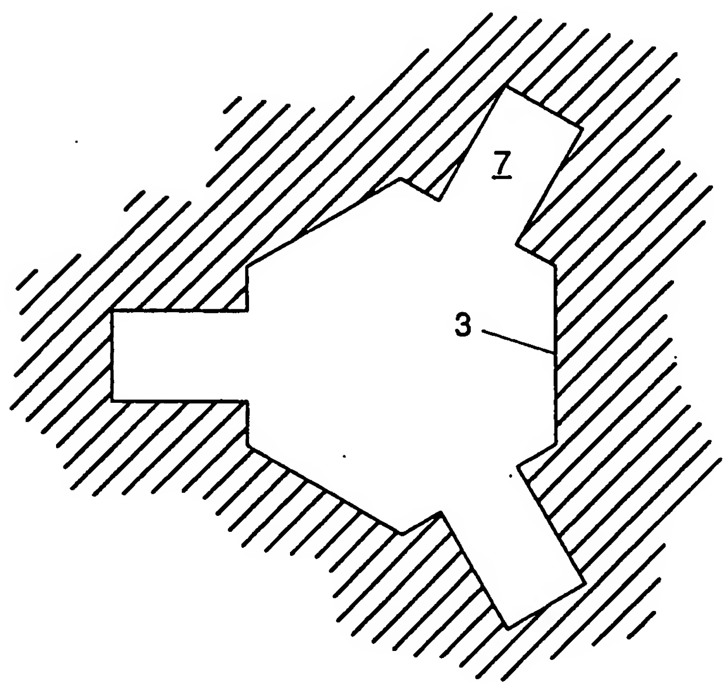

FIG. 2H

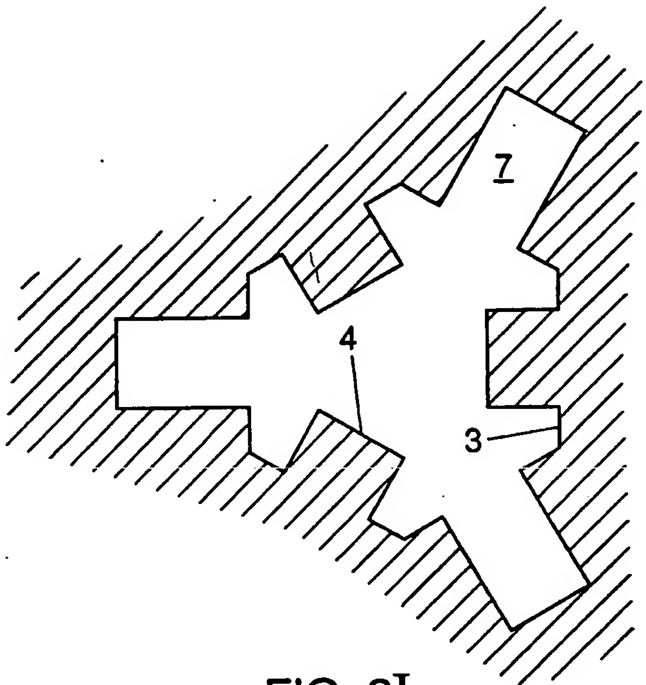

FIG. 2I

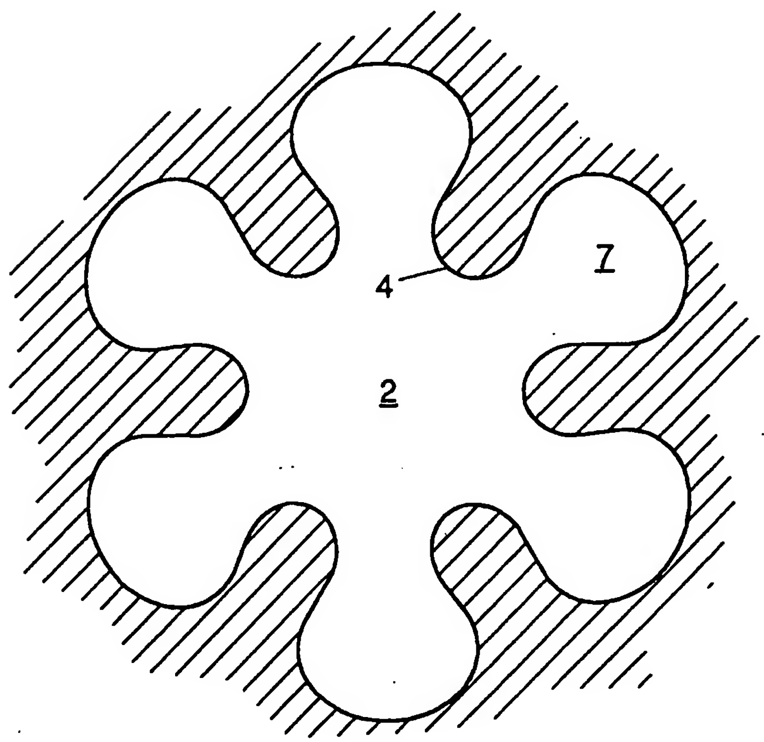

FIG. 2J

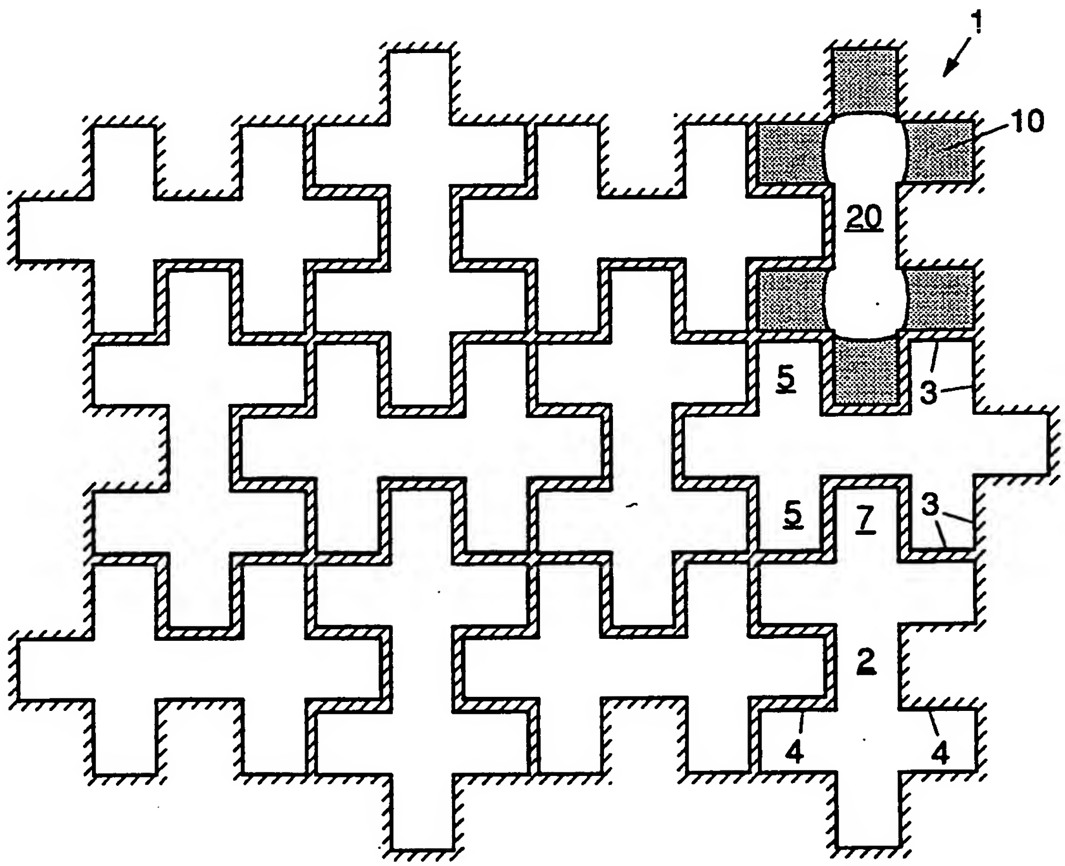

FIG. 2K

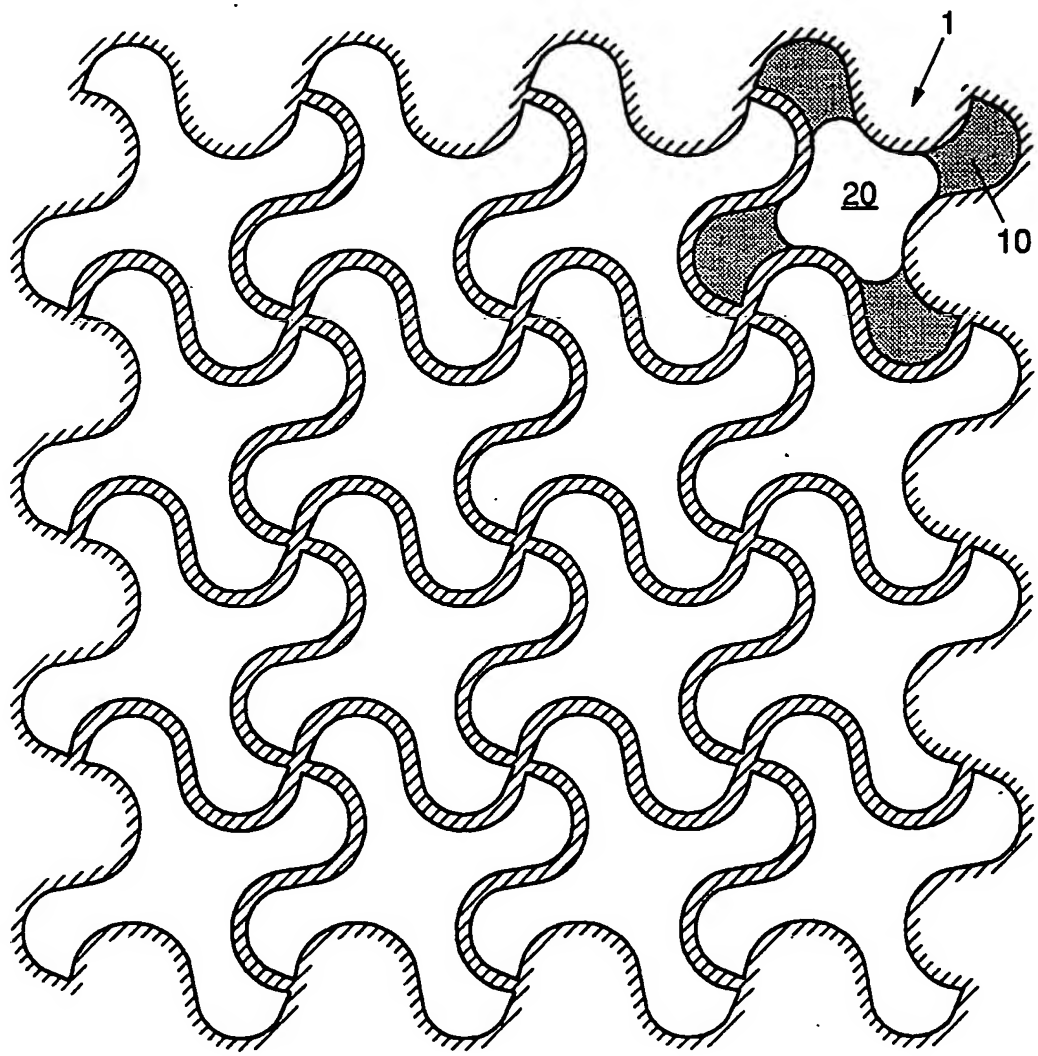

FIG. 2L

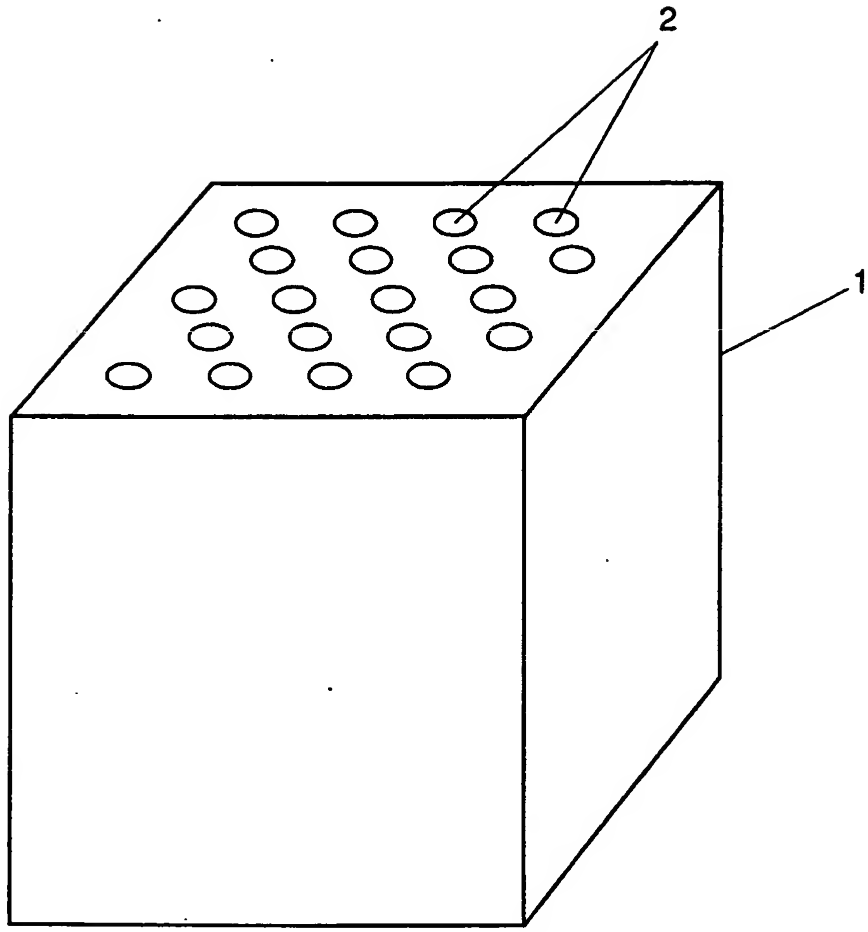

FIG. 3

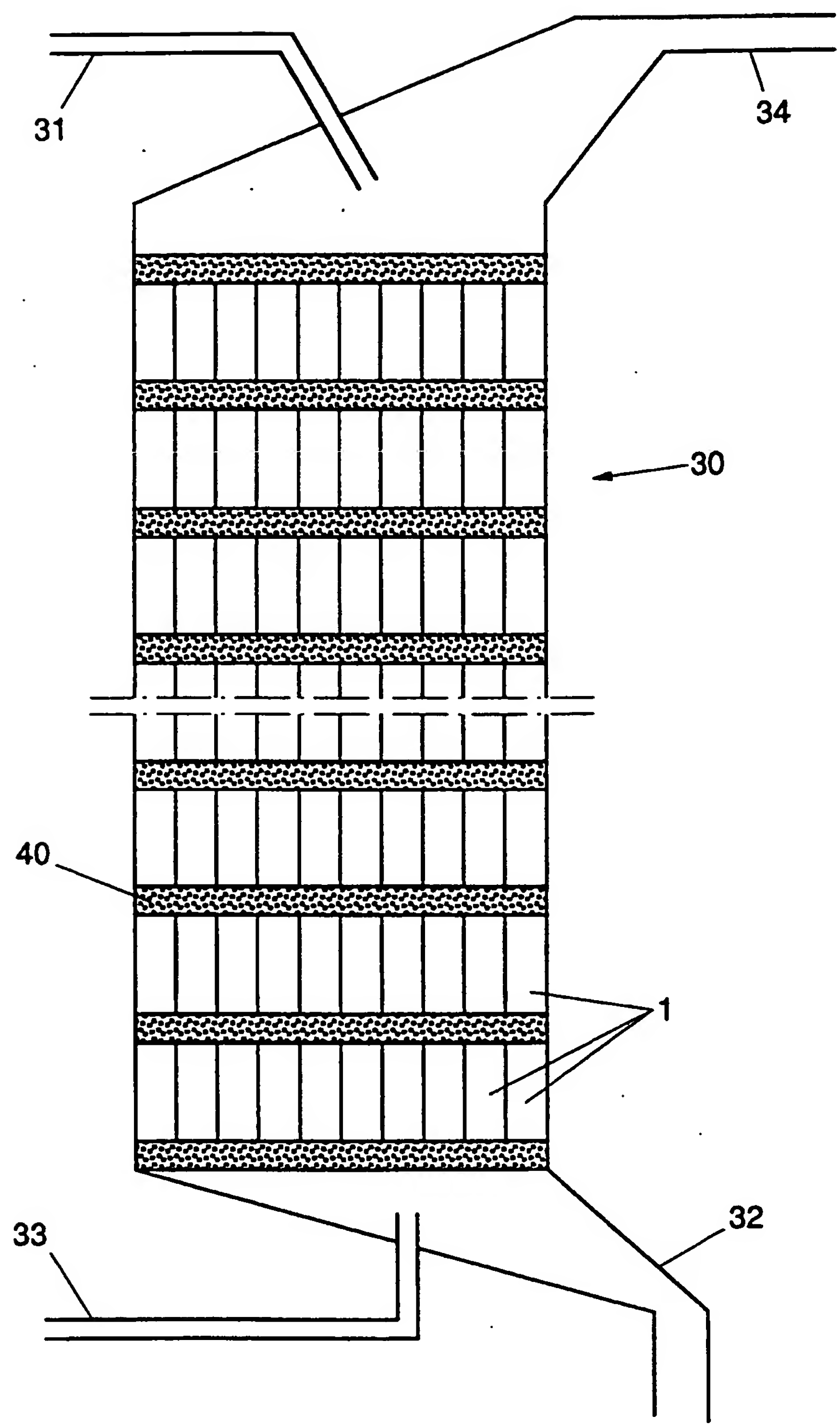

FIG. 4

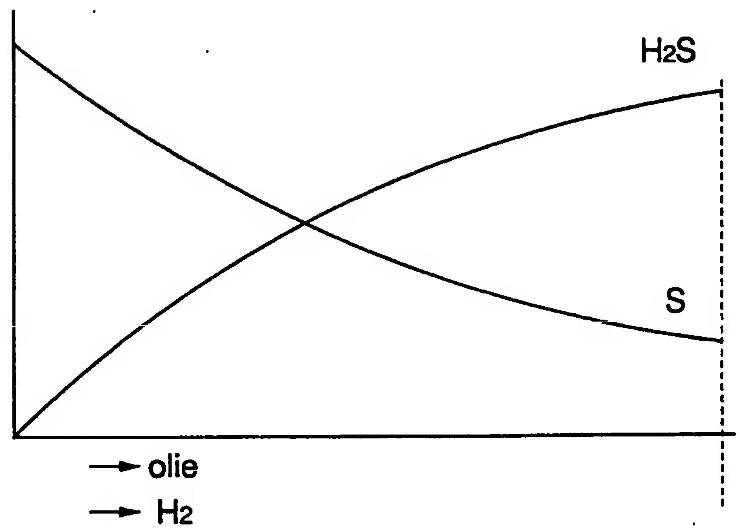

FIG. 5A

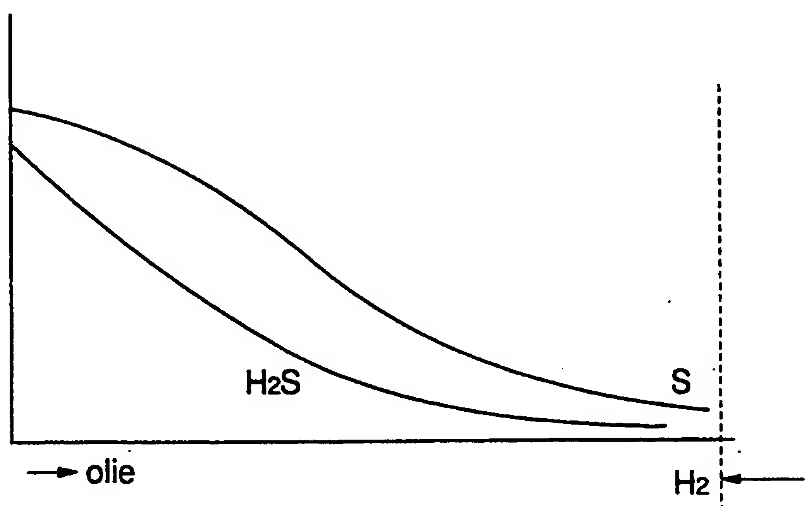

FIG. 5B

INTERNATIONAL SEARCH REPORT

Inter. .nal Application No
PCT/NL 93/00231

A. CLASSIFICATION F SUBJECT MATTER
IPC 5 B01J35/04 B01J35/02 B01J19/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 191 982 (NGK INSULATORS,LDT) 27 August 1986 see claims 1-5; figures 1-3 see page 5, line 29 - page 6, line 16	1-10
Y	EP,A,0 226 306 (IMPERIAL CHEMICAL INDUSTRIES) 24 June 1987 see claims 1,10; figure 8	1-10
A	EP,A,0 279 159 (EMITEC GESELLSCHAFT) 24 August 1988	
A	US,A,4 135 018 (G. E. BONIN) 16 January 1979	
A	FR,A,2 346 048 (CORNING GLASS WORK) 28 October 1977	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 January 1994	25.02.94

Name and mailing address of the ISA	Authorized officer
European Patent ffice, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Thion, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/NL 93/00231

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